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Theoretical study on the nonlinear optical properties of phenylenes and influencing factors[†]

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A systematic investigation of the hyperpolarisabilities of substituted *p*-poly-phenylenes is presented using different quantum mechanical approaches, including density functional theory and Møller–Plesset (MP2) methods. A medium-sized basis set Hartree–Fock (HF) hyperpolarisability calculation based on either a density functional theory (DFT) or MP2 geometry gives reliable results at moderate computational costs when comparing with experimental data. A longer phenylene chain leads to a maximum in the per-unit increase of the investigated property between 3 and 4 repeat units. Changing the underlying geometry from the minimum helix to a planar orientation leads to a significant increase in β, again dependent on the chain length. Terminal *para*-substituents and their influence are studied and categorised. For push–pull groups, the substituent effects are mainly additive, allowing the design of functionalised phenylenes as molecular building blocks for nanofibres with tailored nonlinear optical (NLO) properties. **Copyright © 2008 John Wiley & Sons, Ltd.**

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Keywords: oligo-*p*-phenylenes; nonlinear optical properties; quantum chemical calculations; hyperpolarisability; nanofibres

INTRODUCTION

During the last decade the feasibility of molecular electronics has been demonstrated by studying properties of single molecules in the Ångstrom length scale[1,2] as well as bulk polymeric systems in the micrometer scale. In fact, the latter 'plastic electronics' have resulted in the first commercially available polymer-based light-emitting diodes.[3–5] π-conjugated organic molecules are known to possess attractive optical, electrical and optoelectronical properties.[6–10] Their supramolecular self-assembly processes[11] can give access to defined shape-persistent objects under thermodynamic control which appears to be an alternative to traditional methods and their shortcomings.[12–15] Organic rod-like molecules[16,17] like oligothiophenes,[7,18] perylenes,[19,20] pentacenes[21] and oligo-*p*-phenylenes[22–25] have therefore been studied in the literature both as model systems and applications.[26,27] Phenylenes, like *p*-hexaphenylene, and α-thiophenes, like α-sexithiophene, crystallise as organic nanowires on various substrates after vapour deposition.[28–51] In such fibres, lasing after optical pumping[52–54] and wave guiding[55–57] has been observed. Recent reports have appeared on the synthesis[58] and growth of nanoaggregates[59–61] from the groups of Lützen, Al-Shamery and Rubahn, our experimental collaborators. They have been able to synthesize several substituted quaterphenylenes as monomeric building blocks which form nanofibres after subsequent deposition in vacuum.

It is known that molecules with the electron-donor, π-conjugation, electron-acceptor arrangement (D–π–A) generally exhibit nonlinear optical (NLO) properties.[62,63] Functionalisation of the molecular building blocks – in our case *p*-phenylenes (Scheme 1) – with appropriate donor and acceptor substituents will hence give molecular building blocks for custom-made nanofibres with tailored NLO properties. Varying the number of phenyl rings is another way of tailoring the molecule. When combining the possibility of functionalising the molecule, particularly asymmetric substitution, and varying the number of rings, a large set of possible synthetic targets results. Since not all possible functional groups are readily available for synthesis and an increased chain length poses additional synthetic difficulties due to diminishing solubility, one aim of this study is to design a set of substituents together with the optimal length of the molecular building block which should then guide the synthetic chemists in the preparation of new phenylenes.

The theoretically obtainable property that is to be used to compare structures is the hyperpolarisability (β) as this is directly related to the desired optical properties of the nanofibres. Many theoretical studies evaluating hyperpolarisabilities[64–67] at various levels ranging from semiempirical[68–74] to *ab initio* (SCF, density functional theory (DFT), electron correlation)[75–84] methods have appeared in the literature. A known limitation of

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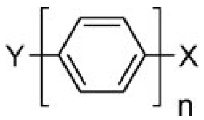
[†] *Dedicated to Professor Curt Wentrup on the occasion of his 65th birthday.*



Scheme 1. *p*-Poly-phenylenes; the chain length is defined as the number of aromatic rings *n*

predicting this property is that the experimentally measured value is dependent on the properties of the individual molecule and on the molecular assembly.[85] However, it seemed reasonable to expect that the predicted β values of the molecular building blocks would provide a good qualitative trend for our goal of molecular design. A study of *p*-hexaphenylene has shown that a coplanar arrangement of the phenyl rings is important for the self-assembly process[86] and for the optical properties. Another purpose of this account is therefore to study the influence of the structure of the phenylenes on the hyperpolarisability. In addition to the above-mentioned goals, this in-depth theoretical study also focusses on determining a method for predicting this property that will allow reliable qualitative comparisons with experimental data.

COMPUTATIONAL METHODOLOGY

All calculations were performed with the programme package Gaussian 03.[87] To determine an adequate theory level several methods and basis sets were compared. Pople's basis set 6-31G(d) [88,89] was used as the default. Larger basis sets (6-311G(d,p) and 6-311G(2d,2p)) combined with the standard Hartree–Fock (HF) method for optimisation and additionally with 6-311G(3df,2pd) were employed to evaluate the influence of basis set on hyperpolarisability. DFT with the B3LYP functional[90,91] and Møller–Plesset (MP2) perturbation theory were also trialled for the optimisations of the ground state geometries. The hyperpolarisability was evaluated using the same theory level as the geometry optimisation as well as HF and MP2 levels of theory with B3LYP optimised geometries. Default values for DFT grid integration, SCF and optimisation thresholds were used. The nature of all stationary points as true minima was confirmed by calculating harmonic frequencies.

Static hyperpolarisabilities ($\omega = 0$) were calculated analytically where available (HF), otherwise (MP2 and B3LYP) a numerical finite-field procedure with the default settings (step size 0.001 a.u.) was employed. A tight SCF energy convergence criterion for all hyperpolarisability calculations was used. The Cartesian hyperpolarisability components in standard orientation from the output were combined to give

$$\beta_{||}(0)_{\text{theory}} = \frac{1}{5}\sqrt{\left(\beta_x^2+\beta_y^2+\beta_z^2\right)}\ ;\ \beta_a = \sum_j \left(\beta_{ajj}+\beta_{jaj}+\beta_{jja}\right).$$ [92]

The aim of our study is to provide a qualitative and reliable comparison between phenylene molecules, as a first approximation the effect of solvation was neglected as it is assumed to cancel for the closely related systems investigated herein.[93,94]

RESULTS AND DISCUSSION

Choice of theoretical level

For calculating accurate quantitative β values it is claimed that relatively large basis sets and post-SCF methods are a necessity.[95] However, recent literature has shown that smaller basis sets such as the double-zeta 6-31G(d) can be relied on to give reasonable qualitative trends.[82–84] DFT methods are known to give reasonably accurate geometries, thermodynamics and vibrational spectra[96] at a low computational cost. However, conventional hybrid methods, such as B3LYP, have been shown to significantly overestimate β values for other π-conjugated push–pull systems.[82] Although there exists new long-range corrected functionals for more accurate prediction of NLO properties they are not yet publicly available.[97–100] In the present study, we evaluated several combinations of methods for the calculation of hyperpolarisabilities and underlying geometries.

Additionally, a previous work[101] has observed correlations between hyperpolarisability and empirical Hammett constants, which is unsurprising given that NLO properties are related to the electronic structure of the aromatic system. Such constants may not provide information on the effect of phenylene chain length; however, they may be useful for predicting the relative substituent effects and were also worth investigating. As there is only a limited number of experimental data on larger substituted phenylenes available we employed known hyperpolarisability values for *para*-disubstituted benzenes and biphenyls to optimise our level of theory (Table 1).

It should be pointed out that the experimental measurement of hyperpolarisabilities is not a trivial one and this task becomes even more complex when examining aggregated systems such as the nanofibres formed from phenylenes. Additionally, different conventions are used for expressing β, depending on the experimental method and conditions, although they are related by linear scaling factors.[92] As our work focusses on qualitative results, and all experimental results herein are derived from the same laboratory and therefore use the same convention, no scaling factors have been applied when comparing with experiment.

For the biphenyls studied the correlation between experiment values and the four test methods (HF NLO properties on HF and B3LYP geometries and MP2 NLO properties on MP2 and B3LYP geometries) were similar (0.91–0.94). Hyperpolarisabilities of substituted benzenes are even better reproduced (0.97–0.98). The Hammett constants (σ_p) also have a reasonable degree of correlation (0.78 and 0.91) indicating that they may be useful as a rough guide for molecular design.

The effect of enlarging the basis set (Table 2) confirms Jacquemin's report[83] that the 6-31G(d) basis set appears to be adequate for predicting NLO properties. It is certainly adequate for our purpose of devising a reliable utility theory level. When applying larger basis sets, only a very slight decrease of the computed hyperpolarisabilities is observed.

Although MP2-derived hyperpolarisabilities are generally considered to be superior due to its electron correlation treatment,[82–84,106,107] all levels of theory give similarly good trends. Taking into account the low computational cost of the HF and B3LYP calculations and the known accuracy of B3LYP geometries (an additional comparison of MP2/ and B3LYP/6-31G(d) geometries of phenylenes shows almost identical data) the HF/6-31G(d)//B3LYP/6-31G(d) level is the obvious choice as the utility theory level combination for the rest of the study.

There is one noteworthy observation in the above data. Typically, our calculated hyperpolarisabilities in Table 1 are larger than the experimental ones, the extent depending on method and on the size of the actual values; smaller number are usually

Table 1. Calculated hyperpolarisabilities ($\beta_{||}(0)$; 10^{-30} esu) in comparison to literature mono and *p*-disubstituted benzene and 4,4′ disubstituted biphenyl values (unadjusted[a] β_{μ} (2ω) EFISH)

Substituents on benzene		Experiment[102]	HF/6-31G(d)// B3LYP/6-31G(d)	HF/6-31G(d)// HF/6-31G(d)	MP2/6-31G(d)// B3LYP/6-31G(d)	MP2/6-31G(d)// MP2/6-31G(d)	σ_p[103,104]
CN	H	0.4^b	0.1	0.1	0.4	0.5	0.66
NO_2	H	1.9^b	1.0	0.7	2.3	2.5	0.78
NO_2	OH	3.0^c	3.8	3.1	7.1	7.3	1.15
OMe	NO_2	5.1^c	4.3	3.5	8.5	8.6	1.05
NH_2	NO_2	9.2^d	6.8	5.5	12.4	11.9	1.44
NMe_2	NO_2	12.0^d	10.4	8.5	19.7	18.3	1.41
Paired correlation^e			0.98	0.98	0.98	0.97	0.91
Substituents on biphenyls		Experiment[105]	HF/6-31G(d)// B3LYP/6-31G(d)	HF/6-31G(d)// HF/6-31G(d)	MP2/6-31G(d)// B3LYP/6-31G(d)	MP2/6-31G(d)// MP2/6-31G(d)	σ_p[103,104]
CN	H	1.9^b	3.7	2.6	5.1	4.7	0.66
C(O)Me	H	2.0^b	5.5	4.2	8.3	7.7	0.50
NO_2	H	4.1^b	8.1	5.4	12.2	11.6	0.78
OMe	C(O)Me	4.9^b	11.3	8.8	18.7	16.5	0.77
CN	OH	6.3^b	6.8	6.8	10.2	11.6	1.03
NO_2	OH	7.7^b	14.3	10.1	22.8	20.2	1.15
OMe	NO_2	9.2^b	15.6	11.0	25.7	18.1	1.05
NH_2	NO_2	24^f	21.3	14.4	34.9	23.6	1.44
NMe_2	NO_2	50^f	29.4	19.2	52.3	39.0	1.41
Paired correlation^e			0.93	0.91	0.94	0.93	0.78

[a] There are different conventions in reporting experimental hyperpolarisabilities,[40] the values given herein are those reported in the original reference.

[bcdf] EFISH measurement as (b) neat or solute in (c) dioxane, (d) acetone or (f) chloroform.

[e] The paired correlation indicates how well a scaled calculated value would predict the experimental value.

strongly overestimated, and there is an approximately ‘cubic drop’ of this effect in biphenyls. However, there are two exceptions to this trend, both concerning the CN substituent (1st and 5th line in the second part of Table 1), where hyperpolarisabilities are calculated relatively too low. The same is found for the benzenes but the limited number of entries does not allow a definite conclusion. It appears that all methods cannot correctly reproduce hyperpolarisabilities of molecules containing a cyano group.

Influence of the phenylene chain length

It has been shown that for linear structures the length of the conjugated system[63] affects the NLO response properties. Some materials have a maximum[108] and other materials show a steadily decreasing benefit of chain length[85] for β. Regardless of which behaviour occurs the property density, which is important for use of the material in a device, will show a maximum because the volume of the phenylene molecules will increase almost linearly with chain length.[68] Experimentally *p*-phenylenes nanofibres become longer with increasing chain length, and the mutual alignment of the nanofibres increases.[109] At the same time the difficulty of preparation and materials handling increases with chain length. When designing a molecule it will therefore be important to find the best trade-off between property density and chain length.

The calculations above used to define the methodology involved substituted benzenes ($n = 1$) and biphenyls ($n = 2$). The investigation was now extended to substituted phenylenes with chain lengths of 4 and 6, and to a limited number of phenylenes

Table 2. Effect of basis set on calculated hyperpolarisabilities (10^{-30} esu) for biphenyls at Hartree–Fock level of theory

Substituents	6-31G(d)// 6-31G(d)	6-311G(d,p)// 6-311G(d,p)	6-311G(3df,2pd)// 6-311G(d,p)	6-311G(2d,2p)// 6-311G(2d,2p)
CN, H	6.8	6.6	6.5	6.4
OMe, NO_2	11.0	10.0	9.7	9.7
NH_2, NO_2	14.4	13.4	12.9	12.8

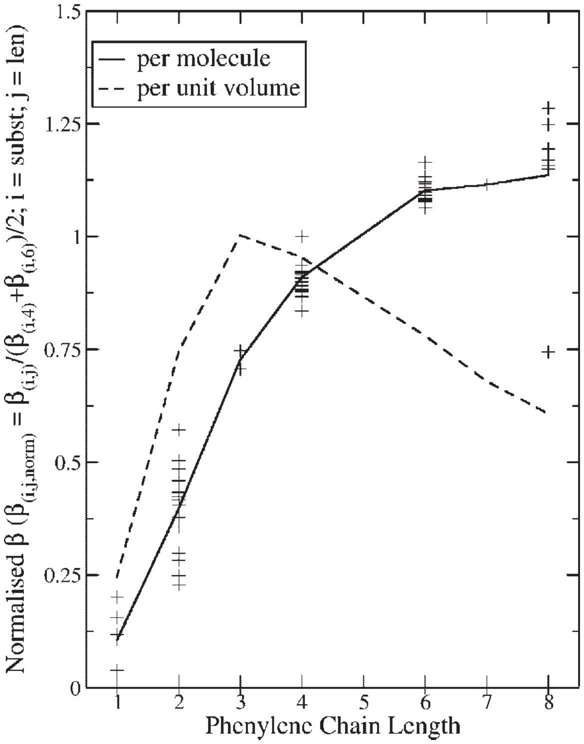


Figure 1. Effect of phenylene chain length on the calculated β, normalised across substituents and for molecular volume

Table 3. Hyperpolarisability β (10^{-30} esu; HF/6-31G(d)//B3LYP/6-31G(d)) and HOMO–LUMO gap (kJ/mol) of different monosubstituted *p*-quaterphenylenes H–Ph_4–X

X	β	HOMO–LUMO gap
H	0.00	428.8
2,5-dimethylpyrrole	0.22	357.9 (420.0)[a]
Cl	0.26	424.0
F	1.54	428.1
OH	6.54	417.9
pyridine[b]	6.91	421.7
OMe	7.25	413.9
SMe	7.50	404.0
NH_2	12.45	397.2
CN	13.42	396.7
C(O)Me	13.57	389.3
COOMe	13.69	401.8
NMe_2	17.91	377.4
NO_2	23.58	338.1

[a] The value in parenthesis is the difference between LUMO and HOMO-1.

[b] Pyridine is used as the fourth aromatic ring (4-Py-Ph_3-H).

with 3 and 8 repeat units. The β values for each phenylene substituent pair were normalised to the average of the corresponding hyperpolarisabilities at $n = 4$ and $n = 6$ (formula in Fig. 1). The known unit cell dimensions of the crystal structure of the unsubstituted molecules[110] were used to normalise for volume (the normalised β is divided by the length of unsubstituted phenylene), allowing comparison by neglecting the volume of the substituents.

As shown in Fig. 1, the predicted hyperpolarisability asymptotically approaches a maximum with the per-unit increase becoming insignificant after $n = 6$. The β density has a maximum for terphenylenes, with only a minor reduction when going to quaterphenylenes. This is similar to the semiempirical results of Morley on *p*-amino, *p*′-nitro-substituted phenylenes[68,111] which showed a maximum at a chain length of 3 and demonstrates its general applicability for donor–acceptor-substituted phenylenes. Given that experimentalists have great difficulties preparing phenylenes with more than four aromatic rings – the solubility decreases dramatically[112] – our results indicate that this is also the optimal chain length for this material.

Substituent effects

The major method of tailoring the optical properties was anticipated to be through varying the substituents. Using a computer allowed us to predict and compare a large range of substituents. The list of substituents employed in the evaluation of a theoretical approach was extended with other known electron-donors or acceptors. Table 3 provides the results obtained for mono-substituted *p*-quaterphenylenes which is considered the optimal length from the previous section. The use of only one substituent will allow us to classify them and to determine whether the effect of a combination of groups is additive.

There are three classes of substituents with low, medium and high influence on the hyperpolarisability. All of them possess an electron-withdrawing effect to some extend. The first three groups in Table 3 (excluding H which leads to a centrosymmetric and hence inactive molecule) appear to have similarly strong $-$I (inductive) and $+$M (conjugative) effects which cancel themselves out and lead to only small β values. For the (thio)alkoxy substituents it is known that the electron-donating conjugation effect dominates the $-$I effect, so that they can be classified as mild pushing groups (with medium NLO properties). Among the strongest substituents with respect to the generated hyperpolarisability in Table 3 are those which have very strong inductive and conjugative effects. All carbonyl group-containing substituents and in particular the nitro and cyano groups are strong pulling groups with large $-$I and $-$M effects. In addition, the amino substituents are dominated by their strong $+$M effect and lead to pronounced electron donation.

As one can expect, the electron-withdrawal and -donation are additive when two opposite effects (push/pull) are present in disubstituted phenylenes. All combinations investigated herein show slightly larger β values (5–15%) than the added total of the individual substituents.[113] It is understandably different when two groups with the same effect are attached to the phenylene; in $\mathrm{MeO{-}Ph_4{-}NH_2}$, the added hyperpolarisabilities (from Table 3) would be 19.7, but the calculated value is only 5.4 10^{-30} esu.

In Table 1, the Hammett constants σ_p, which are known to reflect the donor/acceptor effect of a substituent, show a high degree of correlation between calculated β and the difference between the σ_p values $\left(\left|\sigma_i^p - \sigma_{i''}^p\right|\right)$ for the substituents of each molecule. This comparison has therefore been extended to our

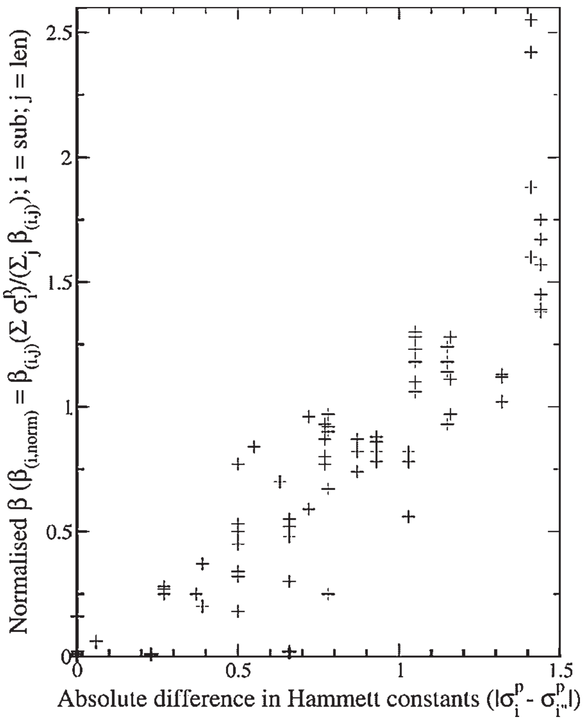


Figure 2. Comparison of the effect of substituents on hyperpolarisability (10^{-30} esu; normalised to chain length) and the corresponding absolute difference in Hammett constants

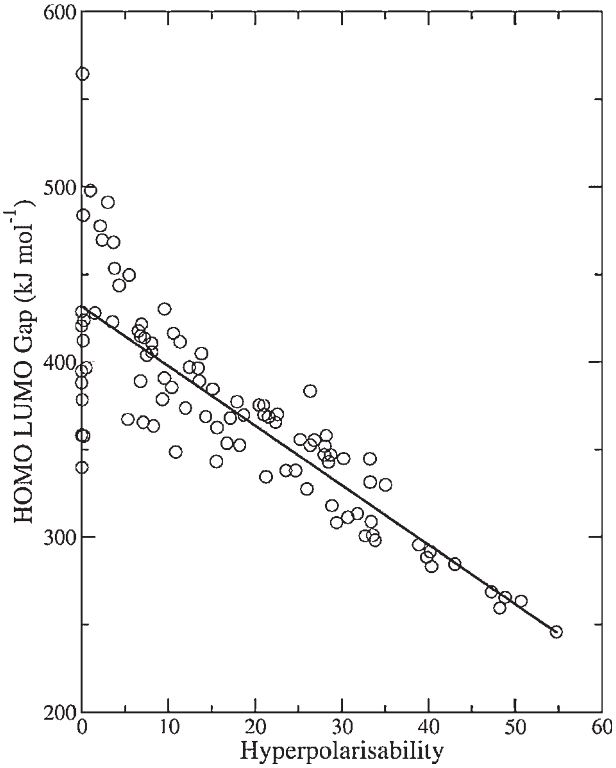


Figure 3. Comparison of calculated HOMO–LUMO gaps (kJ/mol) with calculated hyperpolarisability (10^{-30} esu) for a variety of substituted phenylenes

predictions for chain lengths of 3, 4, 6 and 8, normalised with respect to the effect of chain length. Here again a clear correlation between calculated β and $\left|\sigma_i^p - \sigma_{i''}^p\right|$ is observed (Fig. 2) which (a) corroborates the theory that the hyperpolarisability is influenced by the same electron-donating or -withdrawing effects that are modelled by the Hammett constants and (b) Hammett constants can be applied also to systems with larger conjugated π-systems. As a first approximation, these constants and a chemist's knowledge of the electron donating or withdrawing effect of a substituent are good guides to the effect it will have on the hyperpolarisability at a given chain length.

In Table 3, one can clearly see a general decrease of the HOMO–LUMO gap (as a measure of the band gap, from B3LYP/6-31G(d) optimisations) when going to more 'hyperpolarisability-effective' substituents. The one major exception in this table is 2,5-dimethylpyrrole as terminal substituent. It possesses a different HOMO (π-system of the heterocycle), the comparable orbital containing the conjugated π-system is the HOMO-1 which fits the correlation nicely. Figure 3 contains a comparison of the HOMO–LUMO gap with calculated hyperpolarisabilities across substituent and chain length. A linear correlation is found ($R^2 = 0.71$, gap $= -0.0013\ \beta + 0.164$ across all data points, $R^2 = 0.77$, gap $= -0.0010\ \beta + 0.156$ excluding the short chain lengths which account for the spread of values at the lower hyperpolarisabilities); this demonstrates that the hyperpolarisabilities should be correlated to other properties dependent on the HOMO–LUMO gap such as UV absorption.

Influence of inter-ring angle

One expects that phenylene structures calculated in the gas phase will have some offset angle between adjacent rings. This molecular configuration results essentially from the competition between two antagonistic effects: the repulsion between the *ortho*-H atoms on two adjacent rings and the intermolecular forces which tend to restore planarity. Indeed, the optimised gas phase geometries are always non-planar but on the other hand, X-ray crystal structures of ter- and quaterphenyl show a mean planar structure at room temperature[114,115] which changes to alternating structures at low temperature (110 K; inter-ring angles 26° and (17.1 and 22.7°), respectively). In addition, the only available solid state structure of hexaphenylene also possesses a largely planar structure with herringbone-like packing.[86] Furthermore, a semiempirical study has shown a significant effect of the phenyl torsion on the hyperpolarisability.[116] Here two alternate geometrical arrangements were compared: a helical motif, with each ring offset to its preceding neighbour in the same direction, or a planar structure by constraining the inter-ring angle.

The optimised gas phase structures for the phenylenes have adjacent phenyl rings at an offset angle of approximately 36 ± 2°.[117] This is in accordance with another recent study on chain length and torsion in poly-phenylenes.[118] Phenylene geometries constrained to be planar are energetically less favourable in gas phase though with a larger predicted β. The energetic effect of planarity is relatively independent of substituent: the energy difference between planar and helical structure increases linearly with chain length, with an average increase of 6.7–6.9 kJ mol^{-1} per phenyl–phenyl torsion angle. Table 4 and Fig. 4 show that planarity of a structure increases the hyperpolarisabilities and that this effect intensifies with pheny-

Table 4. The effect on the hyperpolarisability (10^{-30} esu) of planar and helical geometries of the phenylene ring system

Chain length *n*		2		4		6		8	
Substituents		Helical	Planar	Helical	Planar	Helical	Planar	Helical	Planar
C═OMe	H					17.2	32.8		
C═OMe	NH_2					33.3	65.9		
OMe	C═OMe					26.4	51.9		
OMe	NO_2					40.2	82.2		
CN	H			13.4	25.1	18.7	39.5		
OMe	CN			22.6	41.8	28.1	59.1		
H	NO_2	8.1	11.0	23.6	42.2	30.7	62.1	33.9	71.3
NH_2	NO_2	21.3	27.4	40.3	72.7	47.3	96.9	50.7	107.7
OMe	Cl			8.1	16.1				
OMe	H			7.3	12.8				
OMe	NH_2			5.4	9.2				
Average ratio (σ^{n-1})		1.3 (0.04)		1.9 (0.08)		2.0 (0.07)		2.1 (0.01)	

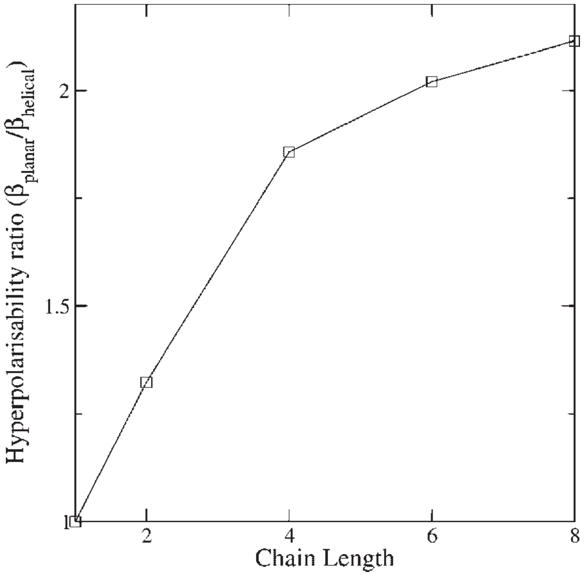


Figure 4. The ratio of hyperpolarisability of planar to helical phenylene structures compared with chain length (from Table 4)

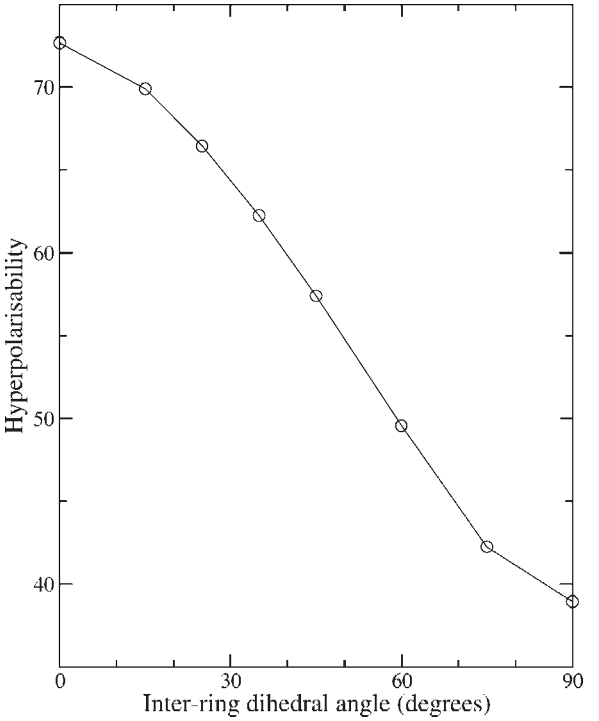


Figure 5. Effect of torsional rotation in NH_2–Ph_4–NO_2 on hyperpolarisability (10^{-30} esu): rotation of the terminal NH_2-bearing phenyl ring from a planar structure

lene chain length, independent of substitution. The effect of having a planar structure and rotating a single, terminal phenyl ring in NH_2—Ph_4—NO_2 is shown in Fig. 5. Here hyperpolarisability falls from 73 to 39 × 10^{-30} esu and follows an approximately sinusoidal shape. As π–π conjugation between adjacent rings is dependent on the inter-ring angle the observed decrease in hyperpolarisability is unsurprising.

A constant ratio of hyperpolarisabilities for helical and planar structures is observed for each chain length *n*, regardless of substitution, and with longer phenylenes it asymptotically approaches a value above 2.1. The consistent sensitivity of the hyperpolarisability to substituent regardless of geometry means that our helical gas phase data will qualitatively predict the substituent effects as long as crystal packing imposes the same structural constraints on the molecules in the nanofibres.

CONCLUSIONS

The qualitative description of hyperpolarisability in polyphenylenes is well described already by the medium-level theory used in this study. It should again be emphasised that our aim is not to accurately reproduce experimental data; instead it is to get a qualitative understanding of the NLO properties of phenylenes. Not surprisingly within our context Hammett σ constants reasonably well describe β but cannot replace calculations for reliable data. Our work confirms and extends the semiempirical work of Morley and co-workers on phenylenes. We also determined the optimum chain length of phenylenes at $n = 3$ or 4 and the influence of the geometrical arrangement, with co-planarity being favourable over the more stable (in gas phase) helical structure, with respect to hyperpolarisabilities. Combining the computationally affordable approach and the results presented here on substituent influence on β with experimental constraints allows the design of phenylenes with tailored NLO properties.

This study solely deals with single molecules and provides a methodology to investigate push–pull phenylenes and their NLO properties. When investigating the building blocks or the nanofibres thereof in a solid state, the interaction between phenylene chains, fibre morphology and orientation become important. Therefore, studies on the interaction between several phenylene chains, the structures of these aggregates and their properties are underway. Given the reliability of our approach, a significant deviation between experiment and prediction will confirm the importance of these structural factors. It will be interesting to see how our predictive approach will perform when derived susceptibilities from SHG experiments of nanofibres made of different quaterphenylenes become available[119] and to see how valid a comparison of a calculated molecular property and one derived from a nanostructured aggregate is.

SUPPORTING INFORMATION

Cartesian coordinates of the B3LYP/6-31G(d)-optimised structures of phenylenes and their energies (in a.u.) as well as raw data used for deriving the figures are available in the Supporting Information.

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[111] Morley's graph has a maximum density at a chain length of 3. The value at a chain length of 2 is close to that of 3. Given that we neglect the volume of substituents (as there are no experimental

data available for the larger number of compounds we use herein) the two studies come to the same conclusion.

[112] This is only true for the herein investigated terminally substituted poly-phenylenes; long alkoxy groups on the phenyl rings improve solubility significantly.

[113] Some of the data are given in Table 4, the remaining results are unpublished.

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